Quantum Mechanics and Atomic Physics

Lecture 10:

Orthogonality, Superposition, Time-dependent wave functions, etc.

http://www.physics.rutgers.edu/ugrad/361

Prof. Sean Oh

Last time: The Uncertainty Principle Revisited

- **Heisenberg's Uncertainty principle:**

$$\Delta x \Delta p \geq \hbar / 2$$

- Position and momentum do not commute

$$[x, p] = i\hbar$$

- If we measure the particle's position more and more precisely, that comes with the expense of the particle's momentum becoming less and less well known.
- And vice-versa.

Ehrenfest's Theorem

- The expectation value of quantum mechanics follows the equation of motion of classical mechanics.
- In classical mechanics

$$\vec{F} = \frac{d\vec{p}}{dt} = -\nabla U, \quad U: \text{potential function}$$

- In quantum mechanics, $\frac{\partial \langle p \rangle}{\partial t} = \langle -\nabla U \rangle$

- See Reed 4.5 for the proof.
- Average of many particles behaves like a classical particle

Orthogonality

- **Theorem:** *Eigenfunctions with different eigenvalues are orthogonal.*
- Consider a set of wavefunctions satisfying the time independent S.E. for some potential V(x)
- Then orthogonality states:

$$\int_{-\infty}^{\infty} \psi_k^* \psi_n \, dx = 0$$

for $k \neq n$ and

$$E_k \neq E_n$$

- In other words, if any two members of the set obey the above integral constraint, they constitute an orthogonal set of wavefunctions.
- Let's prove this…

Proof: Orthogonality Theorem

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + V\psi_n = E_n\psi_n$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_k}{dx^2} + V\psi_k = E_k\psi_k$$

take complex conjugate.

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi_k^*}{dx^2} + V\psi_k^* = E_k\psi_k^*$$

$\Rightarrow$ Multiply by ψ_n

$\Rightarrow$ Mutiply 1st eqn by ψ_k^*

$\Rightarrow$ Subtract:

$$-\frac{\hbar^2}{2m}\left(\psi_k^*\frac{d^2\psi_n}{dx^2} - \psi_n\frac{d^2\psi_k^*}{dx^2}\right) + V\left(\underbrace{\psi_k^*\psi_n - \psi_n\psi_k^*}_{=0}\right)$$

$$= (E_n - E_k)\psi_k^*\psi_n$$

Proof, con't

$$\Rightarrow \quad \frac{d}{dx}\left(\psi_k^* \frac{d\psi_n}{dx} \right) = \psi_k^* \frac{d^2\psi_n}{dx^2} + \frac{d\psi_k^*}{dx}\frac{d\psi_n}{dx}$$

and

$$\frac{d}{dx}\left(\psi_n \frac{d\psi_k^*}{dx} \right) = \psi_n \frac{d^2\psi_k^*}{dx^2} + \frac{d\psi_n}{dx}\frac{d\psi_k^*}{dx}$$

Take diff:

$$\frac{d}{dx}\left(\psi_k^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_k^*}{dx} \right) = \psi_k^* \frac{d^2\psi_n}{dx^2} - \psi_n \frac{d^2\psi_k^*}{dx^2}$$

$\Rightarrow$ Plug into eqn above:

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d}{dx}\left(\psi_k^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_k^*}{dx}\right) = (E_n - E_k)\psi_k^*\psi_n$$

$$\Rightarrow \int_{-\infty}^{\infty} -\frac{\hbar^2}{2m}\, d\left(\psi_k^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_k^*}{dx}\right) = E_n - E_k \int_{-\infty}^{\infty}\psi_k^*\psi_n\, dx$$

$$-\frac{\hbar^2}{2m}\left[\psi_k^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_k^*}{dx}\right]_{-\infty}^{\infty} = E_n - E_k\int_{-\infty}^{\infty}\psi_k^*\psi_n\, dx$$

$\psi_k^* = \psi_n = 0$ @ $\pm\infty$

so left hand side $= 0$

And $E_k \neq E_n$

so,

$$(E_k - E_n)\int_{-\infty}^{\infty}\psi_k^*\psi_n\, dx = 0 \Rightarrow \int_{-\infty}^{\infty}\psi_k^*\psi_n\, dx = 0$$

Theorem is proven

Orthonormality

- In addition, if each individual member of the set of wavefunctions is normalized, they constitute an **orthonormal** set:

If $n = k$, $E_n - E_k = 0$

and integral need not be $\emptyset$.

If ψ_n are normalized:

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx = 1$$

$$\int \psi_k^* \psi_n \, dx = \langle \psi_k | \psi_n \rangle = \delta_k^n$$

$$\delta_k^n = \begin{cases} 1 & (k = n) \\ 0 & (\text{otherwise}) \end{cases}$$

Kronecker delta

Degenerate Eigenfunctions

- If n ≠ k, but $E_n = E_k$, then we say that the eigenfunctions are **degenerate**
- Since $E_n - E_k = 0$, the integral need not be zero
  $$\int_{-\infty}^{\infty} \psi_k^* \psi_n \, dx$$
- But it turns out that we can always obtain another set of Ψ's, linear combinations of the originals, such that the new Ψ's are orthogonal.

Principle of Superposition

- **Any linear combination of solutions to the time-dependent S.E. is also a solution of the T.D.S.E.**
- For example, particle in infinite square well can be in a superposition of states:

We covered this in lecture 4!

$$\psi = c_1 \psi_1 + c_2 \psi_2$$

- T.D.S.E is:

$$H_{sp} \Psi(x,t) = \underbrace{i\hbar \frac{\partial}{\partial t}}_{\equiv H_t} \Psi(x,t)$$

$$H_{sp} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t)$$

So if $\quad H_{sp} \Psi_1 = H_t \Psi_1 \,, \quad H_{sp} \Psi_2 = H_t \Psi_2$

$$\Rightarrow \quad H_{sp}(c_1 \Psi_1) = H_t(c_1 \Psi_1), \quad H_{sp}(c_2 \Psi_2) = H_t(c_2 \Psi_2)$$

$$\Rightarrow \quad H_{sp}(c_1 \Psi_1 + c_2 \Psi_2) = H_t(c_1 \Psi_1 + c_2 \Psi_2)$$

Principle of Superposition II

- Is any linear combination of solutions to the time-independent S.E. also a solution of the T.I.S.E? No!!!

T.I.S.E.: $H_{sp}\psi_1(x) = E_1\psi_1(x)$

$H_{sp}\psi_2(x) = E_2\psi_2(x)$

$$\Rightarrow H_{sp}(c_1\psi_1 + c_2\psi_2) = E_1 c_1\psi_1 + E_2 c_2\psi_2$$

$$\neq E(c_1\psi_1 + c_2\psi_2)$$

  - In other words, linear combinations of eigenstates are not generally solutions of the eigenequation.
  - The measurement will yield either E_1 or E_2, though not with equal probability
  - *The system need not be in an eigenstate* - the superposition state Ψ "collapses" into one of the eigenstates when one makes a measurement to determine which state the system is actually in.

Principle of Superposition III

- If $\psi_i(x)$ are energy eigenfunctions, that is the solution of the T.I.S.E. and the wavefunction at t=0 is given by $\Psi(x,0) = \sum_i a_i \psi_i(x)$, then at a later time t, the wavefunction is given by
- $\Psi(x,t) = \sum_i a_i \psi_i(x) e^{-i\frac{E_i}{\hbar}t}$, where

  E_i is the eigenenergy corresponding to $\psi_i(x)$,

  that is $H\psi_i(x) = E_i \psi(x)$.

  Then, the expectation value of the energy is given by $\langle E \rangle = \sum_i a_i^2 E_i$, (See Reed 4.7 for the proof)

Principle of Superposition IV

- Normalization also requires that

If $\Psi(x,0) = \sum a_i \psi_i(x)$

$\Rightarrow \quad 1 = \sum_i |a_i|^2$

A Time-Dependent Wave-Packet

- See Reed Section 4.8 for a very nice example:

$$\psi = \alpha \psi_1 e^{-i\omega_1 t} + \beta \psi_2 e^{i\omega_2 t}$$

$$\Rightarrow \psi^2 = \alpha^2 \psi_1^2 + \beta^2 \psi_2^2 + 2\alpha\beta(\psi_1 \psi_2) \cos[(\omega_1 - \omega_2)t]$$

$$\omega T = 2\pi$$

$$\Rightarrow T = \frac{2\pi}{\omega_1 - \omega_2} = \frac{2\pi}{(1/\hbar)(E_1 - E_2)} = \frac{h}{(E_1 - E_2)}$$

Normalization gives:

$$\alpha^2 + \beta^2 = 1$$

$$\langle x \rangle = \alpha^2 \int (x\, \psi_1^2)\, dx + \beta^2 \int (x\, \psi_2^2)\, dx + 2\alpha\beta \cos[(\omega_1 - \omega_2)t] \int (x\, \psi_1 \psi_2)\, dx$$

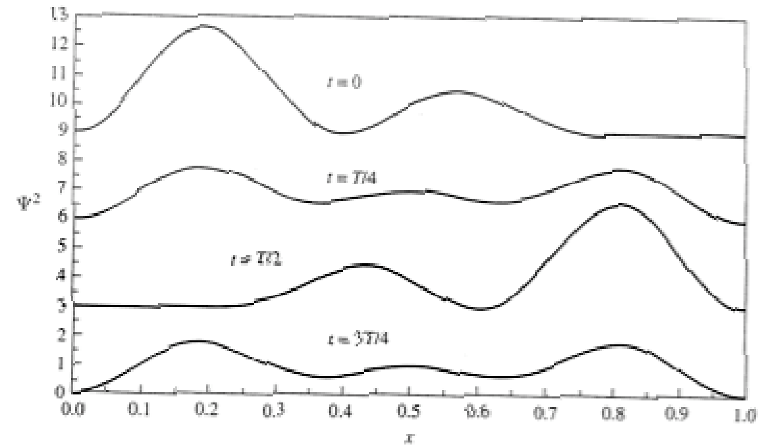

FIGURE 4.3 Time-varying probability-density distribution of a superposition state of the $n = 2$ and $n = 3$ infinite-rectangular well ($L = 1$) wavefunctions with $\alpha = 0.7$ and $\beta = \sqrt{0.51}$. (See Equations 4.8.3 and 4.8.8.) The curves are vertically offset from each other purely for clarity; they should all lie at $\Psi^2 = 0$ at $x = 0$ and 1.

Illustrates concept of a *traveling* wave and the principle of superposition

Measurement and wavefunction collapse

- Consider the infinite potential well problem.
- If at t=0 $\Psi(x,0) = \frac{3}{5}\psi_1(x) + \frac{4}{5}\psi_2(x)$, where
  $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$ for $0<x<L$
- Then at a later time t, $\Psi(x,t) = \frac{3}{5}\psi_1(x)e^{-i\frac{E_1}{\hbar}t} + \frac{4}{5}\psi_2(x)e^{-i\frac{E_2}{\hbar}t}$
  , where $E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$
- At t>0, if you measure the energy of the system, what energy values can you measure with what probabilities?

Continued

$$P(E_1) = \left(\frac{3}{5}\right)^2 = \frac{9}{25}, \quad P(E_2) = \left(\frac{4}{5}\right)^2 = \frac{16}{25}$$

$$P(E_1) + P(E_2) = 1$$

- Now, if your measurement yielded E_1, what is the new wavefunction afterwards?

$\Psi(x,t)$ collapses to $\psi_1(x)$

- Now, after this measurement, if you measure the energy again, what are the possible energy values with what probabilities? E_1 with $P(E_1) = 1$

Measurement continued

- Now if you measure the position of the particle, what position would you measure with what probabilities?

$$P(x) = |\Psi(x)|^2 = |\psi_1(x)|^2 = \left(\sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{L}x\right)\right)^2$$

- Now if your measurement yielded x=4/L, and then if you measure energy again, what energy values are possible?

Theorem

- *If Ψ is in an eigenstate of Q_{op} with eigenvalue λ, then $\langle Q \rangle = \lambda$ and $\Delta Q = 0$.*
- So, λ is the only value we'll observe for Q!
- Proof:

$$\overline{Q} = \langle Q \rangle = \int \Psi^* Q_{op} \Psi \, dx = \int \Psi^* \lambda \Psi \, dx$$

$$\Rightarrow \langle Q \rangle = \lambda \int \Psi^* \Psi \, dx = \lambda$$

$$\overline{Q^2} = \langle Q^2 \rangle = \int \Psi^* Q_{op} (Q_{op} \Psi) \, dx = \int \Psi^* Q_{op} \lambda \Psi \, dx$$

$$= \lambda \int \Psi^* Q_{op} \Psi \, dx = \lambda \int \Psi^* \lambda \Psi \, dx =$$

$$= \lambda^2 \underbrace{\int \Psi^* \Psi \, dx}_{1} = \lambda^2$$

$$\Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2} = \sqrt{\lambda^2 - \lambda^2} = 0$$

- No uncertainty! Observe λ only.

Virial Theorem

- The Virial Theorem (VT) is an expression that relates the expectation values of the KE_{op} and PE_{op} for any potential.
- Suppose operator A is time-independent

$$[A_{op}, H_{op}]\psi = A_{op}(H_{op}\psi) - H_{op}(A_{op}\psi)$$
$$= i\hbar\left[A\frac{\partial\psi}{\partial t} - \frac{\partial}{\partial t}(A\psi)\right]$$
$$= i\hbar\left[A\frac{\partial\psi}{\partial t} - A\frac{\partial\psi}{\partial t}\right] = 0$$

- In VT, A is defined as:

$$A \equiv \vec{r}_{op}\cdot\vec{p}_{op} = -i\hbar\,\vec{r}\cdot\vec{\nabla}$$

- Section 4.9 in Reed goes through the proof of the VT in great detail which gives:

$$\Rightarrow \quad 2\langle KE\rangle = \langle\vec{r}\cdot\nabla V\rangle \quad \text{for any potential } V$$

Example: VT using a radial potential

$$V(r) = k r^n$$

$$\nabla V = \left(\frac{\partial V}{\partial r}\right)\hat{r} = n k r^{n-1}\,\hat{r}$$

$$\hat{r} \cdot \vec{\nabla} V = (r\hat{r}) \cdot (n k r^{n-1})\hat{r} = n k r^n = n V$$

$$\Rightarrow \; 2\langle KE \rangle = n \langle V \rangle$$

VT for Coulomb Potential

Coulomb potential $n = -1$

$$V(r) = \frac{k}{r}$$

$$\langle E \rangle = \langle KE \rangle + \langle V \rangle$$

$$\Rightarrow \langle E \rangle = -\langle KE \rangle$$

and

$$\langle p^2 \rangle = 2m_e \langle KE \rangle \Rightarrow \langle p^2 \rangle = -2m_e \langle E_n \rangle = \frac{\hbar^2}{a_0^2 n^2}$$

Consistent with the Bohr model

$a_0 \equiv$ Bohr radius

Summary/Announcements

- We covered various things today: Orthogonality, Superposition, Measurement, Time-dependent wave function, and various theoems
- Time for quiz: Closed book, and closed note !

- Midterm exam Wed. Oct. 19 in class - it will be **closed book** with a letter size formula-ONLY (no solutions, or extra texts allowed) sheet- Need to turn in together with the answer book.